



Standard Test Method for Organotin Release Rates of Antifouling Coating Systems in Sea Water¹

This standard is issued under the fixed designation D 5108; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the laboratory determination of the rate at which organotin expressed as tributyltin (TBT) is released from an antifouling (AF) coating in synthetic sea water using graphite furnace atomic absorption spectrophotometry (GF-AAS). This does not exclude the use of other analytical methodology for measurement of organotin in sea water such as gas chromatography.

1.2 The values stated in SI units are to be regarded as standard. The inch-pound units given in parentheses are for information only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 7.

2. Referenced Documents

2.1 ASTM Standards:

D 1141 Specification for Substitute Ocean Water²

D 1212 Test Methods for Measurement of Wet Film Thickness of Organic Coatings³

D 4138 Test Method for Measurement of Dry Film Thickness of Protective Coatings by Destructive Means⁴

3. Summary of Test Method

3.1 The candidate paint system is applied to cylindrical test specimens. The coated specimens are placed in a tank of synthetic sea water where the tin levels are kept low by circulating the sea water through a carbon filter. At specified intervals, each specimen is placed in 1500 mL of unused sea water and is rotated for 1 h. The rate of tributyltin release from the paint is determined by measuring tributyltin concentrations in the sea water.

3.2 Analysis of sea water for tributyltin is conducted by extracting the organotin with toluene, washing with sodium hydroxide, and measuring for total tin using (GF-AAS).

4. Significance and Use

4.1 This test method is designed to provide a laboratory procedure to measure changes in the release rates of solvent soluble tin (tributyl- and triphenyltin) that occur during a period of immersion under specified conditions of constant temperature, pH, salinity, and low heavy-metal concentrations in the surrounding sea water. Quantitative measurement of the release rate is necessary to help in selection of materials, in providing quality assurance, and in understanding the performance mechanism.

4.2 This test method serves only as a guide for organotin release rates in service. Organotin release rates of antifouling (AF) paint systems in service can vary over the life of the coating system depending on the formulation and the environment. Differences in berthing locations, operating schedules, length of service, condition of paint-film surface, temperature, pH, and salinity can affect results. Results obtained may not necessarily reflect actual tributyltin release rates that will occur in service, but provide reliable comparisons of the release rate characteristics of different antifouling formulations.

4.3 This test method will serve to characterize the early release rate pattern, as well as estimate the steady state release, of tributyltin from both self-polishing copolymer and free-association antifouling paints.

5. Apparatus

5.1 *Release-Rate Measuring Container*—A 2-L (nominal ½ gal) polycarbonate container,⁵ approximately 13.5 cm (5.5 in.) in diameter and 19 cm (7.5 in.) high, fitted with three polycarbonate rods approximately 6 mm (nominal ¼ in.) in diameter to serve as baffles. Rods shall be evenly spaced on the inside circumference of the container to prevent swirling of water with the test cylinder during rotation. The rods will be secured to the container walls using acetone or methylene chloride.

¹ This test method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.45 on Marine Coatings.

Current edition approved Dec. 5, 1990. Published February 1991.

² *Annual Book of ASTM Standards*, Vol 11.02.

³ *Annual Book of ASTM Standards*, Vol 06.01.

⁴ *Annual Book of ASTM Standards*, Vol 06.02.

⁵ A Nalgene Container, available from Cole-Palmer, 7425 N. Oak Ave., Chicago, IL 60648, catalog number R-6761-20, or equivalent, has been found satisfactory for this purpose.

5.2 *Constant Temperature Bath*—A temperature controlled water bath capable of maintaining a temperature of $25 \pm 2^\circ\text{C}$ into which one or more release rate measuring test containers can be placed.⁶

5.3 *Holding Tank*—A container of such dimensions so as to permit immersion of four or more test cylinders; must be equipped with a system to continuously circulate synthetic sea water in the tank through a carbon filter. The rate of water flow and the size of the carbon filter should be selected to maintain tributyltin concentrations below 100 $\mu\text{g/L}$. Flow rates should generally be set to obtain 2 to 8 turnovers per h. The size and geometry of the tanks as well as the positioning of the inflow and outflow ports for the water circulation system should be selected to obtain a slow, relatively uniform flow of synthetic sea water past all test cylinders in the tank. Maintain the pH of the synthetic sea water between 7.8 and 8.2, and the salinity between 30 and 35 parts per thousand (ppt). The tank shall be provided with heaters to maintain the temperature between 21 and 27°C (70 and 81°F).

5.4 *Test Cylinders*—Approximately 6.4 cm (nominal 2 1/2 in.) outside diameter polycarbonate pipe coated with a 10-cm band of AF paint around the exterior circumference of the test cylinder to provide 200 cm^2 of paint film that can be immersed and freely rotated in the release rate measuring container. Seal the bottom of the test cylinder with a polycarbonate disc using acetone, methylene chloride, or a polycarbonate cement so as to form a watertight joint. Do not coat the bottom 1 to 2 cm of the test cylinder. The test cylinder shall be of such height so that a rotating device can be attached to rotate the cylinder and the upper open end of the cylinder is above the level of the test container immersion liquid to prevent entry of the immersion liquid into the test cylinder.

5.5 *Test Cylinder Rotating Device*—The device shall be capable of rotating the test cylinder in the release rate measuring container at 60 ± 5 r/min. No part of the device shall be immersed in sea water.⁷

5.6 *Centrifuge Tubes*, 50-mL capacity, with screw closures⁸ (or disposable bottles, culture tubes, separatory funnels, etc.) made of polycarbonate, TFE fluorocarbon, or borosilicate glass.

5.7 *Mechanical Shaker*, with appropriate holders.

5.8 *Dispensers*, automatic or repeating, for reagents.

5.9 *Pipets*, with disposable polypropylene tips.

5.10 *Graphite Furnace*, atomic absorption spectrophotometer (GF-AAS) with automatic sampler.

5.11 *pH Meter*, with a mercury/mercurous chloride ($\text{Hg}/\text{Hg}_2\text{Cl}_2$) electrode.

5.12 *Appropriate Volumetric Flasks*.

⁶ Boekel Water Baths, Models 148003 and 148004 available from Boekel Industries Inc., 509-T Vine St., Philadelphia, PA 19106, or equivalent, have been found satisfactory for this purpose.

⁷ A six-paddle stirrer, Model 300, manufactured by Whitaker Medical Mfg. Co., Phipps and Bird Div., 8741 Landmark Rd., Richmond, VA 23228, or equivalent, has been found satisfactory for this purpose.

⁸ Oak Ridge Tubes, available from Cole-Parmer, or equivalent, have been found satisfactory for this purpose.

6. Reagents and Materials

6.1 *Synthetic Sea Water*—Substitute ocean water in accordance with Section 6 of Specification D 1141 or a proprietary equivalent with a salinity of 30 to 35 ppt.

6.2 *Extraction Solvent*—Toluene, spectrograde or equivalent.

6.3 *Tributyltin Standards*—Prepare standards using a stock solution of tributyltin chloride (reagent grade, minimum 96 % pure) in methanol (suggested concentration of approximately 10 mg/L). The standards are acidified with acetic acid (less than pH 4) to obtain a stable solution.

6.4 *Hydrochloric Acid* (HCl) (10 % aqueous solution).

6.5 *Hydrochloric Acid* (HCl) (0.1N).

6.6 *Nitric Acid* (HNO_3) (10 % aqueous solution) can be used in place of HCl to clean labware.

6.7 *Sodium Hydroxide* (NaOH) (3 % aqueous solution).

6.8 *Sodium Hydroxide* (NaOH) (0.1N).

6.9 All reagents and cleaning agents used must be tin-free.

7. Hazards

7.1 *Warning*—Antifouling paints contain toxic materials that could cause skin and eye irritation on contact and adverse physiological effects if ingested or inhaled. In the preparation of test specimens and the application of various types of paints, the use of appropriate protective clothing and equipment is required consistent with local, state, and federal government regulations, and recognized industrial and technical standards. Do not flush spills, overspray, and unused material down the drain, but should be disposed of as hazardous waste.

7.2 See antifouling paint supplier's Material Safety Data Sheet.

8. Calibration and Standardization

8.1 Prepare three standards throughout the range of the quantification limit to 100 μg of tin per litre by dilution in toluene of a stock solution of tributyltin chloride (96 % pure) in methanol. Include one standard with a concentration of approximately 50 μg of tin per litre. An alternate range of concentrations may be used when appropriate.

8.2 Prepare synthetic sea water spiked with three concentrations of TBT in the range of 10 to 50 μg of tin per litre by spiking with stock solution of tributyltin chloride in methanol. When the concentration of tin extracted in toluene exceeds 100 $\mu\text{g/L}$ appropriate dilution should be employed to keep it within the limits of the calibration curve (0 to 100 $\mu\text{g/L}$).

8.3 Operate the graphite furnace in accordance with manufacturer's instructions. Optional conditions are described in Appendix X1.

8.4 Analyze the following:

8.4.1 At the beginning of each instrument run, perform analysis of the toluene blank and standards in toluene in order to establish that the response of the instrument is linear. Plot separate calibration curves for each analysis of the standards (peak height absorbance versus tin concentration), and calculate the slope, intercept, and coefficient of determination for each curve using least squares regression or another appropriate procedure.

8.4.2 *Sea Water Blank*—Extract and analyze as specified for test samples to establish baseline.

8.4.3 *Spiked Sea Water Samples*—Extract and analyze as specified for test samples to determine extraction efficiency. Recovery must be 90 to 110 %.

8.4.4 If changing the graphite tube during a run is necessary, analyze the blank and standards in toluene to ensure proper response and linearity before continuing the sample analysis.

8.5 Determine the tin concentration of individual test samples with reference to the 50 µg/L calibrating standard analyzed immediately after those test samples.

9. Procedure

9.1 Organotins have a strong tendency to adsorb on certain glass or plastic surfaces. Therefore, all labware (glass or polycarbonate) used for organotin release measurements must be treated as follows: clean thoroughly by soaking in 10 % HCl or HNO₃ for a minimum of 6 h. Rinse labware thoroughly with distilled water and allow to dry. Cleaning can also be accomplished by soaking in concentrated HCl for ½ h. Prepare all samples, blanks, and standards in labware treated in this manner. Disposable materials (pipet tips, centrifuge tubes, etc.) do not have to be acid-washed before use.

9.2 Prepare the exposure surfaces (200 cm²) of three replicate test cylinders to provide a suitable surface for adhesion of the paint system to be applied. Mask the surfaces to remain uncoated (including the bottom 1 to 2 cm of the exterior circumferential surface of the test cylinder).

9.3 Paints shall be manufactured a minimum of seven days prior to testing. Also, test paints shall not be allowed to age beyond the manufacturer's recommended shelf life. Provide typical storage conditions during aging, that is, sealed in a container commonly used for sale and held at 20 to 30°C.

9.4 Apply one or more coats of antifouling paint to the exterior circumferential surface of a test cylinder to produce a band of AF paint with an exposure surface of 200 cm² and a minimum dry film thickness of 100 µm (4 mils). Follow manufacturer's instructions with respect to mixing and drying. At a minimum, mechanically shake until the paint appears homogeneous. Apply using a sponge applicator or spray as recommended by the manufacturer. If the paint is marketed only in spray cans, then apply as a spray. After the final application allow the paint to dry for 7 ± 1 days at 23 to 27°C.

9.5 Estimate the initial dry film thickness using a suitable nondestructive method such as Test Methods D 1212. If the leaching tests exceed 6 months measure the film thickness at the conclusion of the test. Methodology for the final measurement can be either that used for the initial measurement of Test Method D 4138. If a nonstandard method is used, make several film thickness measurements for each cylinder and estimate the variability of the determination. Film thickness should remain greater than 50 µm throughout the test. For tests of long duration, the initial thickness may need to be greater than 100 µm to maintain a thickness greater than 50 µm throughout the test.

9.6 Place all cylinders in a single batch in a holding tank after the 7-day drying period. A batch consists of one or more sets of three replicate cylinders coated with a test paint and one control (unpainted) cylinder. The painted surface on the cylinders must be completely submerged. Cylinders must be sta-

tionary and positioned so that sea water moving through the tank will flow around each cylinder.

9.7 Monitor the pH (using a pH meter with a calomel electrode) and the temperature of the synthetic sea water in the holding tank daily. Adjust the pH if necessary using either 0.1 N NaOH or 0.1 N HCl. Quantitate salinity every 14 days and adjust if necessary. Determine TBT concentrations weekly. When TBT levels increase, change the carbon filter before the TBT concentration exceeds 100 µg/L. More frequent monitoring of synthetic sea water may be necessary in some instances to maintain the specified environmental conditions.

9.8 After 1, 3, 7, 10, 14, 21, 24, 28, 31, 35, 38, 42, and 45 days, transfer all cylinders in given batch into individual measuring containers containing 1500 mL of fresh synthetic sea water. Randomly assign cylinders (control and painted) to measuring containers at each leaching. When transferring cylinders, lift the cylinder out of the holding tank, allow sea water to drain off, install the cylinder into the rotating device, and submerge the painted area into the sea water. Immediately start rotation of the cylinder at 60 ± 5 r/min, and continue rotation for 60 min. When transferring the cylinders, do not touch or in any way damage the paint film, and do not allow the paint surface to dry. Complete the transfer as quickly as possible (generally, in less than 5 min).

9.9 If testing beyond the minimum (45 days) length requirement is desired, the study may be extended to 73 days. During the extended test, remove the cylinders from the holding tank every 3 to 4 days to make a measurement of the leach rate.

9.10 At the completion of the cylinder rotation, immediately remove the cylinder from the measuring tank and return it to the holding tank. Pipet a 25-mL subsample of the sea water into a 50-mL centrifuge tube containing sufficient 10 % HCl to reduce the pH to ≤4.0. If the number of samples from the leach measuring steps exceeds the daily analysis capacity, the samples may be refrigerated and stored in the acidified state in a sealed container for up to 14 days. Clean the measuring containers using appropriate procedures (distilled water or acid wash) before reuse.

9.11 Partition acidified sea water samples with 10 mL of toluene (15 min shaking on a mechanical shaker). Remove most of the toluene and wash it with 5 mL of a 3 % aqueous NaOH solution (10 min shaking). Pipet off (or separate using a separatory funnel) the organic phase and analyze for total tin content by GF-AAS. The toluene extract can be stored sealed in the dark at 4°C for up to 24 h before analysis.

10. Calculation

10.1 Calculate the concentration of the TBT cation in the sea water of the measuring container as follows:

$$C_{\text{TBT}} = (C \times E \times F) / S$$

where:

- C_{TBT} = concentration of TBT cation (µg/L),
- C = concentration of tin in the toluene extraction (µg/L),
- E = volume of toluene = 10 mL,
- F = correction factor to convert tin to TBT = 2.5, and
- S = aliquot of sea water analyzed = 25 mL.

This equation can be simplified as follows if the prescribed volume of sea water and toluene are used:

$$C_{\text{TBT}} = (C_{\text{Sn}} \times 10 \times 2.5)/25 \\ = C_{\text{Sn}}$$

10.2 Calculate the release rate by the following formula:

$$R = (C_{\text{TBT}} \times V \times D)/(T \times A)$$

where:

R = release rate ($\mu\text{g}/\text{cm}^2/\text{day}$),

D = 24 h/day,

V = 1.5 L, volume of sea water in measuring container,

T = 1 h during which cylinder is in measuring container, and

A = 200 cm^2 surface area of paint film.

This formula can be simplified as follows:

$$R = (C_{\text{TBT}} \times 1.5 \times 24)/(1 \times 200) \\ = C_{\text{TBT}} \times 0.18$$

10.3 Calculate the 14-day cumulative release of TBT cation as follows:

$$R = R_1 + (2 \times R_3) + (4 \times R_7) + (3 \times R_{10}) + (4 \times R_{14})$$

where:

R = 14-day cumulative release, $\mu\text{g}/\text{cm}^2 \cdot 14$ days, and

$R_1, R_3, R_7, R_{10},$ and R_{14} = release rates for sampling days 1, 3, 7, 10, and 14, respectively, $\mu\text{g}/\text{cm}^2$ per day.

10.4 Calculate the average release rate ($\mu\text{g}/\text{cm}^2$ per day) by averaging individual release rate measurements taken from day 21 through the last day of sampling (day 45 through day 73). If values at day 21 are high and it is suspected that the release had not reached pseudo steady-state conditions, then compare the release rate at day 21 to the mean for all release rates from day 21 through the termination of testing (45 to 73 days). If the release rate exceeds the mean by two or more standard deviations, then the release rate may be excluded from the average. If the day 21 release rate is excluded, the day 24 release rate may be evaluated by the same procedure.

11. Report

11.1 Report the following information:

11.1.1 Report the concentration in micrograms per litre of TBT cation in the sea water of the measuring tank and the rate of TBT cation release (micrograms per square centimetre per day) for each sampling time (give values for individual replicates as well as the mean). Plot the rate of TBT release as a function of time (use linear axes). Also report the 14-day cumulative release and the average release rate.

12. Precision and Bias

12.1 Precision and bias for this test method have not been determined.

13. Keywords

13.1 antifouling coating system; organotin; release rate; TBT; tributyl tin

APPENDIXES

(Nonmandatory Information)

X1. GRAPHITE FURNACE OPERATING INSTRUCTIONS

X1.1 Operate the graphite furnace in accordance with the manufacturer's instructions. Table X1.1 and Table X1.2 provide guidelines that have been used by two operators.

TABLE X1.1 Navy Equipment—for Toluene Extraction

NOTE 1—Light Source: Tin electrodeless discharge lamp (EDL)
Wavelength: 224.6 nm
Background Corrector: On

Step	Temperature, °C	Ramp Time, s	Hold Time, s	Gas Flow (mL/min)
1. Dry	100	5	10	300
2. Dry ^A	110	5	5	300
3. Char ^B	1000	10	2	300
4. Atomize	2000	0	8 ^C	0
5. Clean	2700	2	5	300
6. Cool	20	2	15	300

^A 286.3 nm tin hollow cathode.

^B Gas stop stage must be used after Step 2 to prevent the carrier gas sweeping organotin out of the tube.

^C Stop gas.

TABLE X1.2 Perkin-Elmer 4000AS⁸ Fitted With A Perkin-Elmer 500 Graphite Furnace With Temperature Programmer

NOTE 1—Light Source: Hallow cathode lamp
Wavelength: 286.3 nm

Step	Temperature, °C	Ramp Time, s	Hold Time, s
1. Chart ^A	250	7	30
2. Ash	900	7	30
3. Atomize	2600	0	5
4. Clean	2700	1	3

^APurge gas used: argon.

X2. AUTOSAMPLER

X2.1 *Perkin-Elmer AS40 Autosampler*⁹—This autosampler has been used with the Perkin-Elmer HGA 500 graphite

furnace. The autosampler introduces aliquots of 20 µL into the graphite tube. Each sample is analyzed three times and an average given. The machine automatically recalibrates after every 12 samples.

⁹ Available from Perkin-Elmer Corp., 761-T Main Ave., Norwalk, CT 06859-0001, or equivalent, has been found suitable for this purpose.

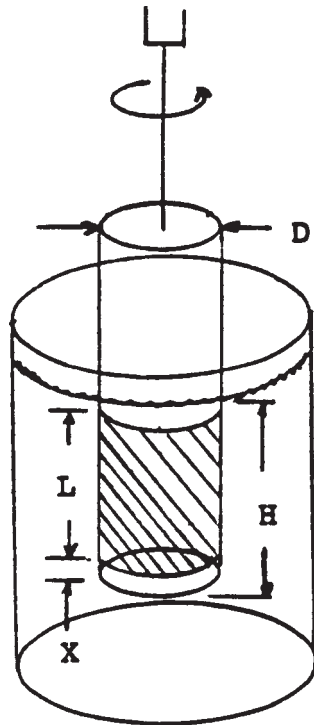
X3. SUGGESTED TABULAR REPORT FORM

Aliquot	Day	Rotation Time, h	Measured Concentration of Tin, µ g/L				Avg TBT Release Rate, µ g/cm ² per day	Total Release Rate, µg/cm ² per sample interval	Cumulative Total TBT Release Rate, µg/cm ²
			Rep 1	Rep 2	Rep 3	Average			
1	1								
2	3								
3	7								
4	10								
5	14								
6	21								
7	24								
8	28								
9	31								
10	35								
11	38								
12	42								
13	45								
14	to 73 days (optional)								

X4. DESCRIPTION OF PROPOSED TESTING APPARATUS

X4.1 A 200 cm² organotin antifouling paint film of a minimum 100-µm thickness is applied to the curved surface of a polycarbonate cylinder closed at one end (see Fig. X4.1). This cylinder is suspended with its closed end immersed within and concentric with a larger polycarbonate cylinder holding

synthetic sea water. The coated internal cylinder is rotated about its axis at 60 ± 5 r/min in order to produce a peripheral speed of about 1 knot. In practice, the commercially available polycarbonate “multipurpose jars” described in this test method will hold 1500 mL of synthetic sea water.



NOTE 1—*Test Container Dimensions:*

Capacity, L	2
Inside diameter, cm	12.7
Outside diameter, cm	13.3
Height (without cover), cm	19

NOTE 2—*Rotating Test Cylinder Dimensions:*

D	= approximately 7 cm (2 1/2 in. nominal),
H	= 12 cm min,
L	= 10-cm coated section, and
X	= 1-cm uncoated band.

FIG. X4.1 Dimensions of Testing Apparatus (Container and Cylinder)

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